

***In Situ* X-Ray Studies of Ferroelectric Thin Films**

SCIENTIFIC ACHIEVEMENT:

Using a unique *in situ* metalorganic chemical vapor deposition facility that we have developed at BESSRC Sector 12-ID of the Advanced Photon Source, we have investigated the growth and properties of the prototypical perovskite ferroelectric lead titanate (PbTiO_3), synthesized as thin films with thicknesses from 5 unit cells to 100 unit cells (S.K. Streiffer, J.A. Eastman, D.D. Fong, Carol Thompson, A. Munkholm, M.V.R. Murty, O. Auciello, G.R. Bai, and G.B. Stephenson, PRL **89**, 067601 (2002)). We have experimentally demonstrated for the first time that epitaxially-strained PbTiO_3 grown on strontium titanate substrates exists in a non-centrosymmetric (ferroelectric) tetragonal phase as much as 200°C above the bulk ferroelectric-to-paraelectric phase transition temperature, approaching the theoretically predicted value of 752°C (Pertsev *et al.*, PRL, **84**, 3722 (2000)) for film thicknesses of approximately 100 unit cells. However, the phase transition temperature is observed to decrease with decreasing film thickness, as expected if the polarization at the interfaces is intrinsically suppressed relative to its equilibrium value in the bulk. Data from the x-ray scattering experiments also show for the first time that depolarization-induced 180° stripe domains form in ferroelectric thin films, as evidenced by evolution of distinctive satellite features around PbTiO_3 Bragg peaks. Two stripe domain phases are found, which differ in their domain wall structure. Finally, by analyzing the variation of stripe period with film thickness, we have been able to extract the 180° domain wall energy.

SIGNIFICANCE:

Oxide piezoelectric and ferroelectric thin films are used or envisioned for numerous diverse applications such as sensors, actuators, and non-volatile memories. Although stripe domains having long been expected to occur in ferroelectric thin films and are postulated to affect their properties dramatically, there has been no direct evidence of their formation before this work. The observed stripe phase is an excellent example of how novel ordered ground states may arise from chemically-induced, substrate-induced, or field-induced interactions in complex materials. Competition between these different interactions can be exploited to yield instabilities that enhance the sensitivity of the local atomic and electronic structure to a stimulus field. Our rapidly increasing ability to tailor three-dimensional nanostructures offers the promise of developing new ways to control and utilize novel ground states as well. The present work demonstrates that nanostructuring via thin film processing has the potential for controlling and significantly enhancing ferroelectric performance. For example, the observation of strain-elevated ferroelectric transition temperatures could lead to the development of actuators that could operate in higher-temperature environments. The ability to monitor structure *in situ* during thin film processing is also critical for property optimization. Because the films were grown under identical conditions, and the growth itself was monitored *in situ*, detailed and quantitative comparisons can be made for a range of properties. Most importantly for the field of ferroelectric films, our data provide one of the first truly comprehensive investigations of ferroelectric film properties as a function of thickness and temperature in the nanoscale thickness regime.

PERFORMERS:

S.K. Streiffer, D.D. Fong, J.A. Eastman, O. Auciello, P.H. Fuoss, G.B. Stephenson, Carol Thompson (Northern Illinois University and ANL)

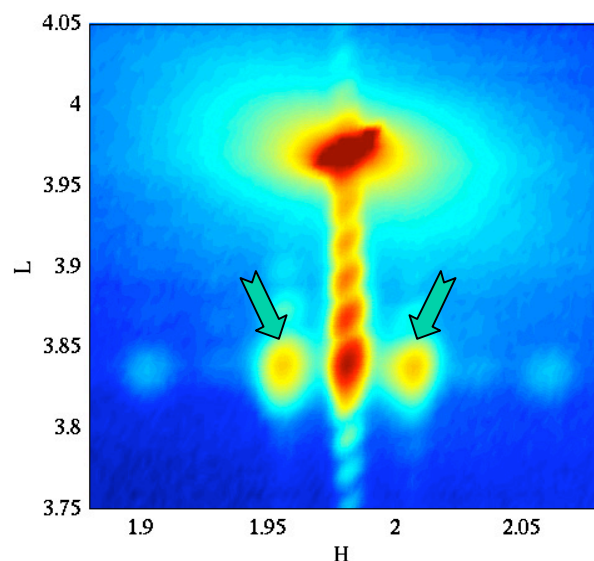
FWPs: 58307, 58926

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- **Ferroelectric properties are a strong function of film thickness and strain.**

- We have used *in-situ* synchrotron x-ray scattering to determine the ferroelectric transition temperature in epitaxial PbTiO_3 thin films grown on SrTiO_3 . For thicker films, we find a substantial increase in T_c due to strain, in agreement with the mean-field prediction of $\Delta T_c = 260^\circ\text{C}$ for an infinitely thick film[†]. T_c is postulated to be lower in thinner films because of an intrinsically reduced ferroelectric polarization at the film interfaces.

[†] following Pertsev et al., PRL, **84**, 3722, (2000)

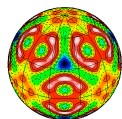
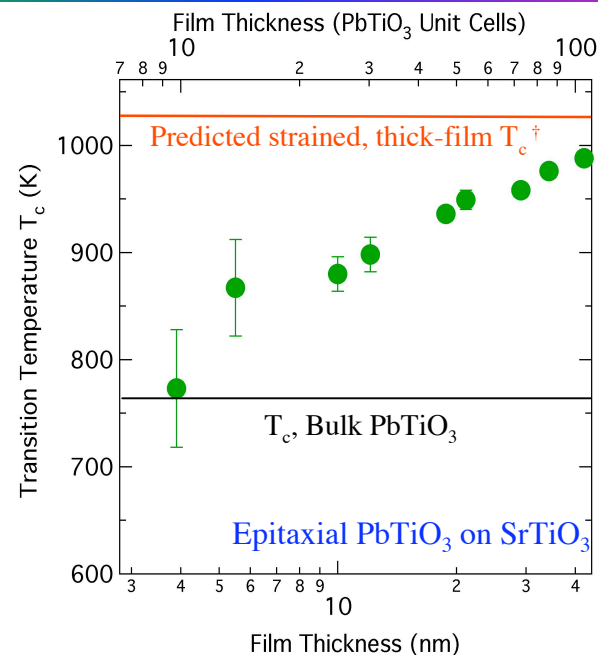


- **Epitaxial ferroelectric films order to balance competing driving forces.**

- We have observed for the first time x-ray diffuse scattering (arrowed) around the PbTiO_3 Bragg peak in epitaxial films, arising from highly periodic 180° polarization stripe domains.
- Polarization stripes arise from competition between domain wall and depolarization energies. Although predicted, they have never before been demonstrated to exist in ferroelectric thin films.

This work is reported in S.K. Streiffer, et al., PRL **89**, 067601 (2002)

Performers: S.K. Streiffer, D.D. Fong, J.A. Eastman, O. Auciello, P.H. Fuoss, & G.B. Stephenson, C. Thompson (NIU, ANL)



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